Gas Diffusion and Dielectric Studies of Polystyrene–Fullerene Compositions

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ABSTRACT: Polystyrene–fullerene compositions containing up to 0.45 mol % (3 wt %) fullerene C_{60} were investigated. It was established that the addition of fullerene to polystyrene (PS) leads to an increase of molecular packing density and so influences the transport of small molecules through the polymer films. Gas diffusion through films of PS–fullerene compositions is slower than through PS films, and gas separating properties of compositions are higher. Dielectric studies showed that the fullerene is distributed as clusters in the polymer matrix of solid composition prepared from a toluene solution of PS and fullerene. Heating without air to the temperature higher than PS glass transition leads to increasing relaxation time of α-transition in PS of compositions containing >0.15 mol % (1 wt %) fullerene. This effect is caused by rather strong interaction of PS chains via fullerene molecules entered into the PS–fullerene complex. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 85: 2946–2951, 2002

Key words: composition; fullerene; polystyrene; dielectric relaxation; gas transport

INTRODUCTION

Discovery of fullerene molecules consisting exclusively of carbon atoms and development of technology for their integrated synthesis have given rise to making new fullerene-containing materials for electronics, laser engineering, optics, biology, and medicine.[1–4] A new line of inquiry has focused on the synthesis and study of fullerene–polymer systems, which can be divided in two types. The first is compounds in which the fullerene–polymer covalent bonds are realized. The other type is compositions in which donor–acceptor or hydrophilic–hydrophobic interactions between the polymer and fullerene take place.

Polystyrene (PS) is one of the first polymers that was successfully modified by fullerene.[5–17] Various approaches were used for obtaining fullerene-containing PS; for examples, processes of free-radical and anionic polymerization or preparation of compositions. Free-radical polymerization of styrene in block or in an aromatic solvent leads to formation of a dark brown polymer when fullerene exits the reaction vessel.[5,6] Anionic polymerization through the formation of fullerene-containing PS «alive» active centers results in complex "star-shaped" and "dumbbell-like" structures. The mechanism of the anionic polymerization has been investigated in detail.[7–12] The formation of a composition with coordination bonds between PS and fullerene has been considered in the work of Sushko et al.[13]

In most works, the problems of synthesis of fullerene-containing PS as well as determination of the optical and physical properties of the complex have been mainly examined in the solvent state.[13–17] However, more complete evaluation of the practical value of fullerene-containing PS requires studying not only its properties in solutions but also the basic parameters responsible

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for its behavior in the solid state. The mode of interaction between the fullerene and PS, and also the influence of both components on structural and kinetic parameters of the PS–fullerene system determines the physical properties of the polymer material.

The purpose of the present work was to study properties of PS–fullerene compositions in the solid state by gas diffusion and dielectric relaxation. The objects of research were films obtained from dilute solutions of PS and fullerene.

EXPERIMENTAL

Materials

Fullerene extract containing >98 wt % C_{60} was purified from moisture traces by heating to 100 °C in vacuum. For film preparation, fullerene was dissolved in a toluene solution. PS (MW = 320 10^{-3}) was also dissolved in toluene. Then, toluene solutions of C_{60} and PS were mixed in the required quantity. PS–C_{60} films (30 μm thick) were obtained by toluene evaporation on a cellophane surface at 40 °C. PS–C_{60} compositions contained 0.5, 1.0, 2.0, and 3.0 wt % C_{60} (0.075, 0.15, 0.30, and 0.45 mol % C_{60}, respectively; where mol % C_{60} = quantity of C_{60} moles: quantity of PS monomer units).

Density Determination

The density (ρ) of films was determined by a flotation method in a saccharose solution at 25 °C. The molecular packing coefficient (k) determines the fraction of the occupied volume.[18] It was calculated from eq. 1,

$$k = \frac{N\sum_i \Delta V_i}{M}\rho \tag{1}$$

where N is Avogadro's number, M is the molecular weight of a monomer unit, and $\Sigma\Delta V_i$ is the volume of a monomer unit calculated as sum of group contributions.

Gas Transport Research

Gas separating properties were investigated on a gas chromatography installation with a diffusion type cell by air transmission at 30 °C and a partial pressure of ~1 bar. The data of the analysis were used for calculation of O_2 and N_2 permeability coefficients and selectivity of their separation on the membrane.

Dielectric Measurements

The temperature–frequency dependence of tgδ for PS–C_{60} compositions containing from 0 to 0.45 mol % C_{60} were investigated. Before measurement, film samples were dried in vacuum at 40 °C for 4 h. Dielectric measurements were carried out at a frequency range from 0.1 to 100 kHz in a vacuum sealed glass cell with pressure brass electrodes at 1.3 Pa and a temperature range 20–150 °C. After the first measurement, the samples were cooled and re-measured in the same temperature–frequency range.

RESULTS

A light scattering study of solutions has shown that PS and fullerene form aggregates with coordination bonds.[13] Usually, as a result of aggregate formation, the structure of the polymer chains can become more compact or, conversely, looser. To elucidate the structural changes in PS macromolecules after C_{60} addition, we compared the film density of PS and that of composition containing 0.30 mol % C_{60}. The obtained density values (1.051 and 1.069 g/cm^3, respectively) made it possible to calculate molecular packing coefficients of 0.662 and 0.668, respectively. This result established that the addition of C_{60} leads to a more compact structure of polymer.

Gas Transport Properties

Transport of small molecules through a polymer film is a method sensitive to change in the polymer packing density. Gas transport is estimated quantitatively using the gas permeability coefficient (P_i) and the selectivity (α). The gas i permeability coefficient is given by

$$\bar{P}_i = \frac{V \cdot l}{A \cdot \tau \cdot \Delta p} \tag{2}$$

where V is the gas volume, l is the membrane thickness, A is the membrane area, τ is the time of gas permeation, and Δp is the pressure gradient between the membrane sides. Gas separation is based on different permeability of the membrane for the gas mixture components. Selectivity in the separation of two gases is determined by:

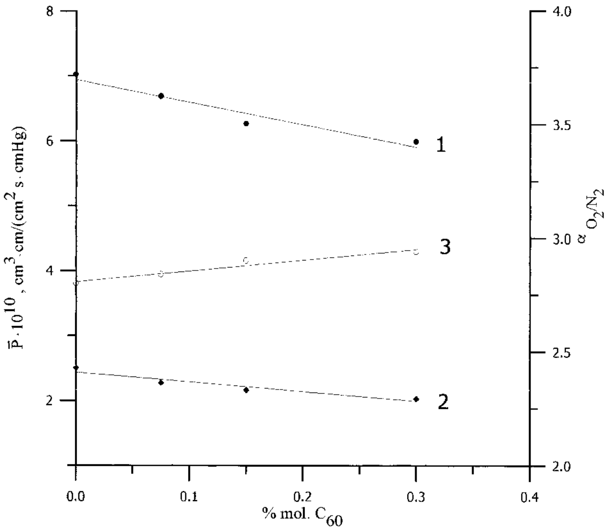

Figure 1 Permeability coefficients of (1) O_2, (2) N_2, and (3) selectivity versus C_{60} content in PS–C_{60} compositions.

$$\alpha_{i/j} = \frac{\bar{P}_i}{\bar{P}_j} \tag{3}$$

The results of determination of O_2 and N_2 permeability and selectivity of their separation for PS and its compositions containing from 0.075 to 0.30 mol % C_{60} are shown in Figure 1. As evident from the figure, the transition from pure PS to compositions leads to a decrease in gas permeability coefficients, which is accompanied by increasing in selectivity of air separation into O_2 and N_2. These results testify that gas-separating properties are improved in PS–C_{60} compositions.

Dielectric Properties

Assessment of the dependence of C_{60} molecule distribution in the polymer medium on the concentration was made by studying molecular mobility. For this purpose the method of dielectric losses and polarization was used. This method is informative because the molecular mobility in the polymer systems is sensitive to intra- and intermolecular interactions. Polarization development (i.e., the establishment of predominant dipole orientation in the direction of external electric field) takes place as a result of the thermal motion of macromolecules. Therefore, polarization requires a certain amount of time (relaxation time). Depending on the ratio of external field frequency to relaxation time, either statistic polarization or the process of its establishment is observed. The latter has the form of dielectric permittivity dispersion and that of the region of maximum tangent of dielectric losses angle (tgδ). The study of temperature–frequency dependence of tgδ makes it possible to evaluate a relaxation time (τ) and to calculate the activation energy (ΔU) of dipole polarization by eqs. 4–7:

$$\tau = 1/2\pi f_{\max} \tag{4}$$

where $f_{\max}$ is the frequency at which tgδ passes through a maximum at a given temperature,

$$\tau = \tau_o e^{(\Delta U)/RT} \tag{5}$$

where τ_o is the constant, R is the universal gas constant, and T is the experimental temperature.

Taking a logarithm of eqs. 4 and 5, one obtains

$$\log\tau = \log\tau_o + \frac{\Delta U}{2.303RT} \tag{6}$$

$$\log f_{\max} = \log\frac{1}{2\pi\tau_o} - \frac{\Delta U}{2.303RT} \tag{7}$$

The ΔU value may be treated in terms of potential energy of internal rotation in the macromolecular chain only when the cooperativity of dipole polarization relaxation is low. This case is valid for local processes (ΔU = 4–15 kcal/mol). For relaxation processes related to the backbone chain motion in the highly elastic state (α-process, ΔU = 30–150 kcal/mol), the activation energy is treated as apparent and is interpreted as the temperature coefficient of relaxation time, $d\tau/d(1/T)$. High ΔU values are determined by the cooperativity of α-transition. This cooperativity consists of the concerted motion of the chain monomer units (intramolecular interaction) and that of adjacent molecules (intermolecular interaction).

In the PS–C_{60} system, it is intermolecular interactions that determine the difference in the mobility of polymer chains surrounded by similar chains or being in contact with C_{60} molecules.

The dielectric behavior of PS is well investigated.[19] It is a slightly polar glassy polymer that shows relaxation dielectric losses only in the field of transition into the highly elastic state (α-transition). Far from the absorption maximum of the given relaxation process, tgδ is of the order of 10^{-4}.

The temperature–frequency dependences on tgδ of PS and its compositions containing 0.075 and 0.15 mol % C_{60} are shown in Figure 2. The same relaxation region of dipole polarization related to α-transition in PS is observed for all three samples. It can be seen from this figure that the addition of fullerene to PS slightly reduces the temperature of dielectric absorption peak and enhances its intensity. The heating of samples during measurements higher than the PS glass transition temperature (80 °C) without access to air does not change temperature of tgδ $_{\max}$, but results in appreciable changes in the intensity (Figure 2b).

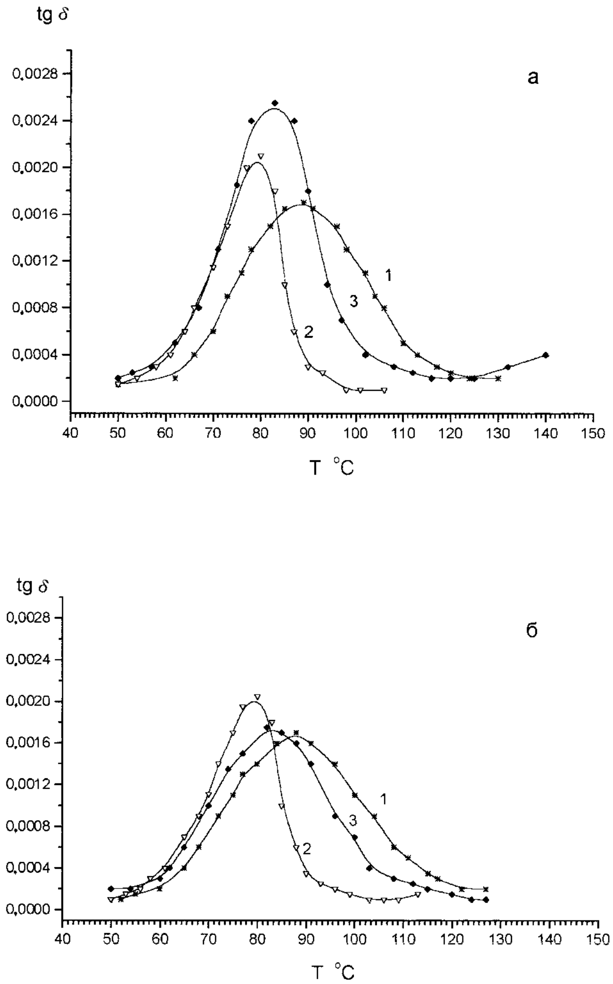

Figure 2 Temperature dependence of tgδ for PS–C_{60} compositions containing (1) 0 mol % C_{60}, (2) 0.075 mol % C_{60}, and (3) 0.15 mol % C_{60}, (a) before heating and (b) after heating to 150 °C without air (frequency, 0.1 kHz).

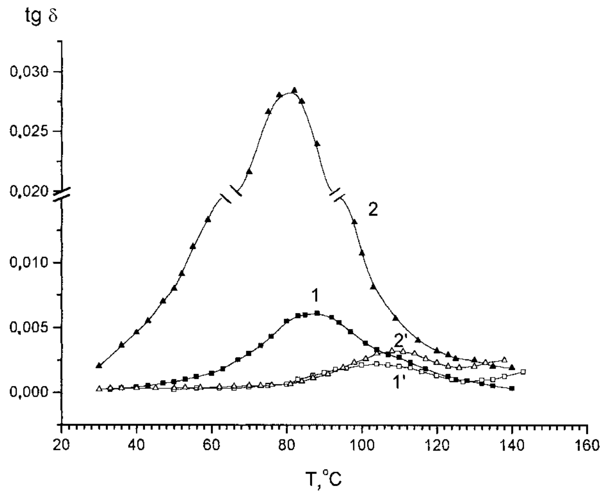

Figure 3 Temperature dependence of tgδ for PS–C_{60} compositions containing (1,1') 0.30 mol % C_{60} and (2,2') 0.45 mol % C_{60}, (1, 2) before heating and (1', 2') after heating to 150 °C without air (frequency, 0.1 kHz).

Samples containing 0.30 and 0.45 mol %C_{60} show essential changes in tgδ = $\phi(T)$ dependence (Figure 3). A new relaxation range of dielectric losses appears close to the PS glass transition temperature. Its intensity increases with the C_{60} content in the composition and greatly exceeds the α-transition intensity in PS. Heating to 130 °C results in the suppression of intensity of this dielectric absorption peak. For heated samples containing 0.30 and 0.45 mol % C_{60}, only one peak of tg$\delta_{\max}$ is observed. Its height is close to that of α-transition in PS, but its relaxation time is higher (Figure 3). The apparent activation energy of α-transition for heated samples of PS–C_{60} compositions was obtained from dependencies $\log f_{\max} = \phi(1/T$; Figure 4). It is equal to 65–79 kcal/mol.

The dependencies of activation energy (ΔU), relaxation time (τ), and temperature position of tg$\delta_{\max}$ ($T_{\max}$) on C_{60} content in compositions are plotted in Figure 5 from the data of Figures 2–4. The course of $\log \tau = \phi$ (mol % C_{60}) and $T_{\max} = \phi$(mol % C_{60}) dependencies is nonmonotonic. If the relaxation time of α-transition in PS was equal to 10^{-4} s, the addition of 0.075 mol % C_{60} decreases τ to 10^{-5}s. Subsequent increase in C_{60} amount in the composition leads to an increase in τ. For the 0.045 mol %C_{60}–PS sample, the relaxation time of α-transition is equal to $5 \cdot 10^{-2}$ s (T = 100 °C). The changes in ΔU are equal to ~14 kcal/mol and tend to increase.

DISCUSSION

The obtained data can be treated as a reflection of molecular interactions between PS and fullerene. The addition of C_{60} to PS leads to increase of molecular packing density of PS chains, which influences the transport of small molecules through polymer films. Gas diffusion through PS–C_{60} composition films is slower than through PS films, and gas separating properties of compositions are higher.

The character of changes in PS–C_{60} compositions was observed by the dielectric method by comparing the $\mathrm{tg}\delta = \phi(T)$ curves for initial samples and samples after thermal treatment. It is known[20] that fullerene in solution can be in the cluster state. It may be assumed that in the PS–C_{60} solid compositions before heating, fullerene is also distributed as clusters in polymer matrix. Hence, the difference in $\mathrm{tg}\delta = \phi(T)$ curves of PS and its compositions is related to the mobility of dipolar units of fullerene clusters, the kinetic characteristics of which are determined mainly by the C_{60}–C_{60} interaction. The question of the mechanism of dipole relaxation in fullerene is debatable. As stated in some works,[21,22] oxygen impurity is the basic that the dominant contribution brings. Other works showed that dielectric characteristics of fullerene are their internal properties and only slightly depend on impurities.[23,24]

It is evident that the heating of compositions leads to the destruction of fullerene clusters, as demonstrated by the absence of high-intensity relaxation transition in $\mathrm{tg}\delta = \phi(T)$ curves for heated samples. It is possible to suggest that at the temperature when PS is in a high-elastic state, the destruction of fullerene clusters facilitates more uniform distribution of components in the system and the formation of PS–C_{60} aggregates. As a result, the plastification phenomenon takes place in compositions with 0.075 and 0.15 mol % C_{60} (Figures 2 and 4). Being inserted between PS chains, the fullerene molecules weaken interchain interaction and reduce polymer glass transition temperature. An increase in the relaxation time of α-transition in PS with increase of C_{60} content can evidently be explained as follows. C_{60} molecules are capable of strong intermolecular interaction because of a lot of conjugate links in the C_{60} structure.[25] When C_{60} content is >0.15 mol %, the chance of interaction between C_{60} molecules in the PS–C_{60} system may increase and lead to physical linking of PS chains.

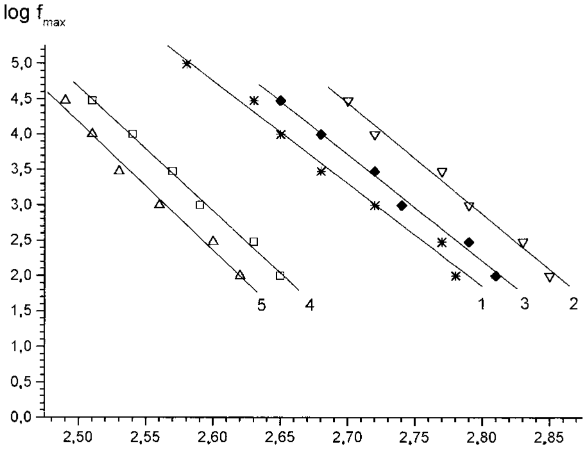

Figure 4 Dependence of $\log f_{max} = \phi(1/T)$ for PS–C_{60} compositions containing (1) 0 mol % C_{60}, (2) 0.075 mol % C_{60}, (3) 0.15 mol % C_{60} , (4) 0.30 mol % C_{60}, and (5) 0.45 mol % C_{60}, after heating to 150 °C without air.

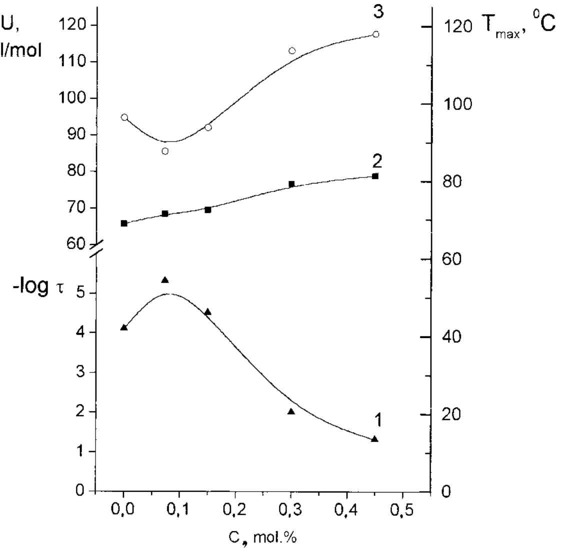

Figure 5 Dependence of (1) relaxation time (τ), (2) activation energy (ΔU), and (3) temperature position of $\mathrm{tg}\delta_{max}$ (T_{max}) on C_{60} content in compositions after heating to 150 °C without air (frequency, 0.1 kHz).

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